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THE IDENTIFICATION AND INVESTIGATION
OF THE EXPANSION CHARACTERISTICS
OF CLAYS BY X-RAY DIFFRACTION

KEITH H. DEARTH AND
RICHARD C. WILLIAMS

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THE IDENTIFICATION AND INVESTIGATION
OF THE
EXPANSION CHARACTERISTICS OF CLAYS
BY X-RAY DIFFRACTION

Submitted to the Faculty of
Rensselaer Polytechnic Institute
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by
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and
RICHARD C. WILLIAMS

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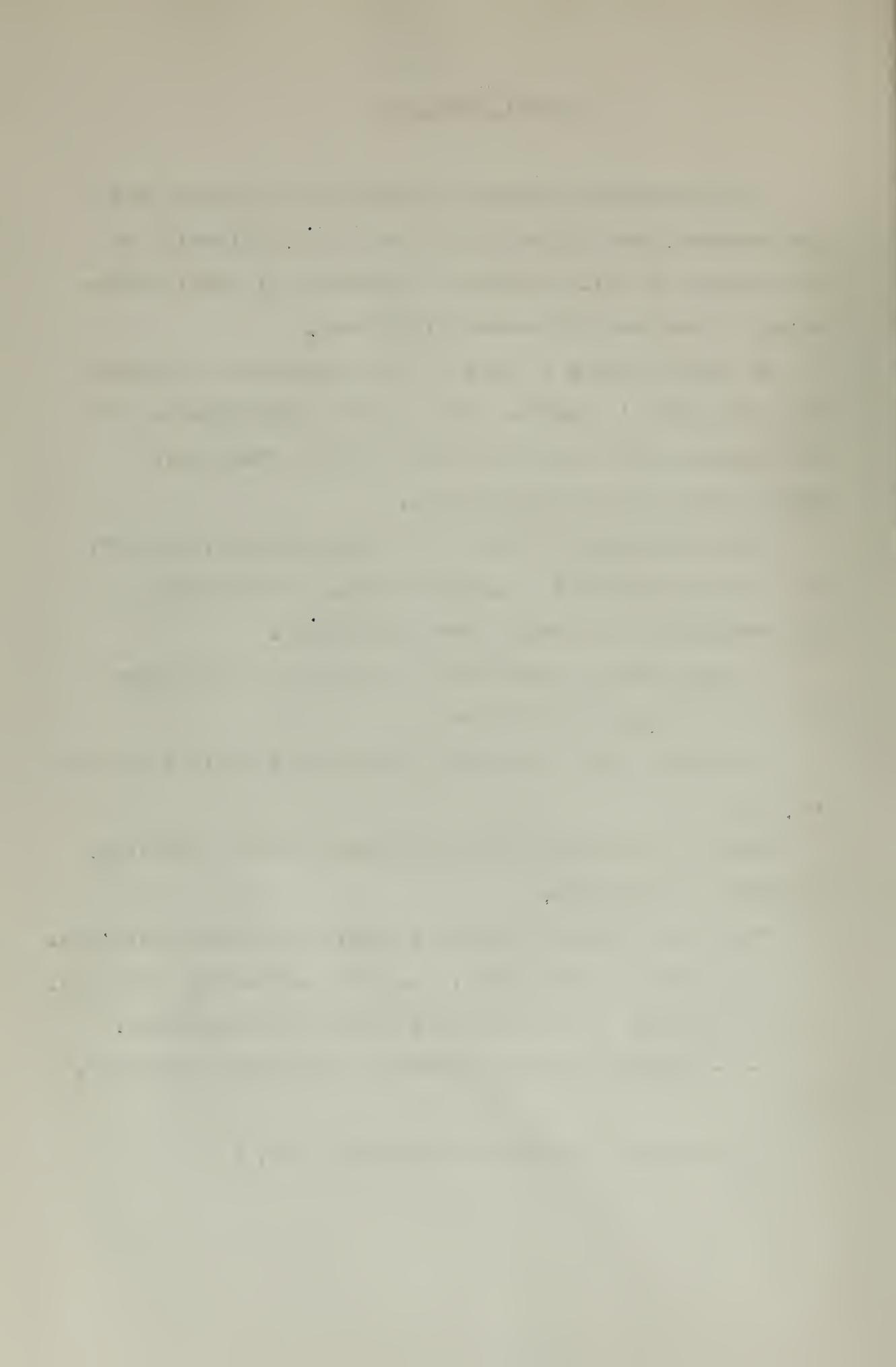


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PART I
INTRODUCTION

INTRODUCTION

During the thirty-nine years since Laue discovered that x-rays interact with crystalline materials to give diffraction effects, x-ray diffraction has become an exceedingly valuable tool to industry and research. The chemist and physicist as well as the mineralogist have found, in x-ray diffraction, a powerful adjunct and often a substitute for more costly and time consuming analyses. The metallurgist recognizes x-ray crystal structure analysis as the outstanding contribution of the science of physics to the study of alloys. X-ray diffraction has permitted the soil scientist to make some of his greatest strides toward a more complete knowledge of soil make-up and behavior.

In 1930, using x-ray diffraction, Hendricks and Fry discovered that the clay materials of soil were crystalline. This was definitely confirmed in 1931 by Kelley, Dore and Brown and these discoveries led directly to the identification of specific substances establishing them to be composed principally of given clay minerals⁽⁶⁾. Since that time, investigators have used x-ray diffraction to study the crystalline structure of the clay minerals, to establish a system of their precise identification, to study the hydration characteristics and behavior due to the wetting of expanding lattice clays, and to study the

base exchange mechanism of clays.

Quantitative analysis by x-ray diffraction has been put to extensive use in the field of chemistry and it is believed that the same can be achieved in the soils field.

The principal objective of this thesis was the development of a good TECHNIQUE for the x-ray diffraction of clays such that the penetration and reflection of x-rays were a maximum with a minimum amount of exposure giving a clear and complete diffraction pattern. This entailed: (1) Arriving at an optimum clay particle size; (2) establishing a procedure whereby the clay sample, both dry and then fully hydrated, was easily prepared for mounting in the x-ray camera so as to have the proper shape, size and consistency; (3) choosing the most advantageous x-ray target material and the optimum radiation line and series of that material; (4) determining the proper x-ray photographic film and exposure time; and finally, (5) proper interpretation of the resulting diffraction pattern so as to determine the identification of the clay and study its expansion characteristics due to the effects of homo-ionic saturation and hydration.

Such research is not new as it has been done many times before, and numerous results have been published. However, very little information has been published covering the actual procedures followed and what methods of sample preparation were used. Practically no data is offered in these published results which enable us to

determine such essential information as particle size, specimen size, ion content of clay, moisture content and origin of clay. Without such information available, the results are of no practical value.

With the above criticisms in mind, it was decided to make it a subsequent objective of this thesis to establish a definite procedure for the x-ray diffraction of clays which can be readily followed and applied toward future investigations of soils incorporating such possibilities as identifying and measuring the components making up the soil, determining the state of chemical combination of the constituent elements, determining the nature of the adsorbed ions, and obtaining an indication of the processes involved in the deposition, consolidation, and induration of the soils.

PART II

THEORY

THEORY

All crystalline matter is composed of atoms or molecules arranged in such a manner that they form definite families of planes in various directions through the crystal. By considering primary x-rays to be reflected by these planes in the face of the crystal, the Braggs⁽¹⁾ were able to reduce Laue's original mathematically complex analysis of this interaction between x-rays and crystalline matter to terms of great simplicity. In figure 1, two such planes AB and CD represent one of the many families of planes found in a crystal. Two rays emf and gnoph of the defined x-ray beam are shown to be partly reflected from these planes when striking them with an incident and reflected angle of θ . According to the laws of optics⁽²⁾, these reflected rays must be in phase to be observed as a reflection. Consequently, ray gnoph must be longer than ray emf by an integral value of the wave length λ . Inspection reveals that this path difference is the distance nop and that $no = d \sin \theta$, and $op = d \sin \theta$; thus $nop = 2d \sin \theta = n\lambda$, which is the statement of Bragg's law⁽³⁾: "A given wave length will be reflected in a given spectral order only when the glancing angle takes a unique value θ ".

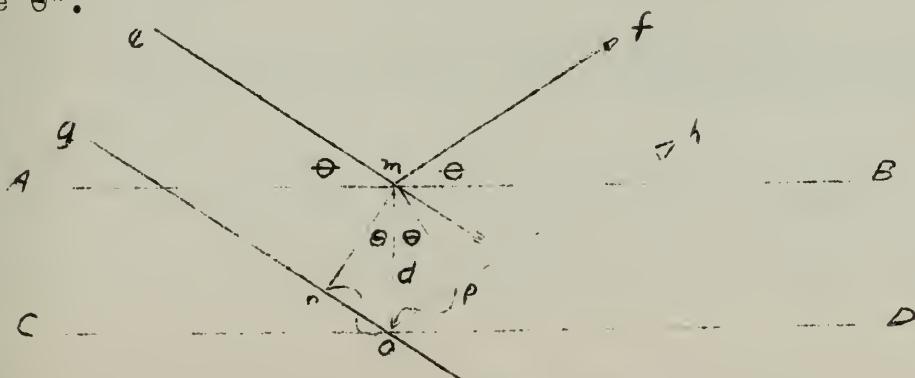


Figure 1. Reflection of x-ray beam from planes in face of crystal

The formation of a reflected beam is conditioned by the existence of equally spaced layers of particles, but not upon the regular spacing of these particles within the layers.

Those sets of net planes which are densely populated commonly occur as crystal faces and emit high intensities of reflection whereas those net planes of sparse population do not occur as face planes and emit low intensities of reflection.

A crystal is essentially a pattern. The atoms are arranged according to a plan, such that the same configuration is repeated at regular intervals in all three dimensions. When a pattern is three dimensional, as in a crystal, the array of points at which the pattern repeats is a "space-lattice". By joining the points space can be divided into a series of parallel-sided unit cells each of which contains a complete unit of pattern. The whole structure is formed by stacking unit cells side by side. The volume of each unit cell is the same.

The axes of the unit cell are designated as a, b and c as shown in figure 2.

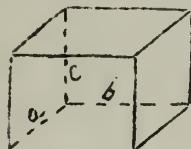


Figure 2. Unit Cell

The edges of the unit cell are termed "unit translations" in the pattern.

The various planes of a crystal are designated by their intercepts (h, k, l) on the reference axes a, b, c respectively.

ly. A plane which is perpendicular to the c -axis and parallel to the a and b axes is designated as a (0 0 1) plane.

Those points of the space-lattice at which the patterns of a crystal repeat are occupied by atoms and are termed "lattice particles or points". Any plane of a crystal which is occupied by lattice points is known as a "crystal plane" or "net plane". A crystal face is always parallel to a net plane.

External crystal faces are parallel to the more densely crowded net planes of the space lattice.

Spherical waves are created when x-rays, which are electromagnetic waves, cause forced oscillations of the planetary electrons of the atoms which they traverse, the electrons absorbing energy from the x-rays when moving away from the nucleus and radiating energy in all directions when moving toward the nucleus. The dimensions of the space-lattice are of the same order of magnitude as the wave lengths of x-rays and this three-dimensional point system will produce very narrow pencils of rays only in those directions in which these spherical waves are in phase. These reinforced waves are the rays that produce the individual spots in x-ray patterns (Laue, rotation, Weissenberg, etc.) obtained from single crystals. If the single crystal is replaced by a large number of smaller crystals, that is, a powder, their statistical orientation, unless preferred orientation effects result owing to peculiar crystal shapes, then must produce a whole series of such discrete pencils, so that as a result a continuous diffraction cone is obtained. If this cone is now re-

corded on a photographic film placed perpendicular to the cone axis, the diffraction effect is obtained as a line which is in the form of a ring. A pattern on which the diffraction rings from all families of planes have been recorded is usually referred to as a powder pattern and consists of a series of concentric rings on a flat film, or axes of rings on a cylindrical strip of film.

A fixed space arrangement of atoms with definite fixed distances between them must always produce precisely the same x-ray pattern. Furthermore, if the same space arrangement is retained but the distances between atom centers are changed, the x-ray pattern will retain its same general appearance but will either expand or contract. On the other hand, if the space arrangement is altered, the pattern is changed. Consequently, x-ray diffraction patterns are a sort of finger-print of crystalline materials. Each individual substance present in a mixture will produce its unique diffraction effects, so that the pattern derived from the mixture is a composite of the patterns of all the materials or compounds in the mixture. Furthermore, the intensities of the lines of the individual patterns are a function of the relative amount of the material present in the mixture, so that the method also has quantitative aspects.

The clay minerals offer a fascinating field of study for x-ray analysis, the exploration of which has only been commenced. The typical minerals are micaceous in structure, consisting of thin hexagonal flakes with perfect cleavage. There can be little doubt that all are based upon the sheet

of linked tetrahedral groups which is characteristic of the mica minerals.

The principal constituents of the lattices of the various clay minerals are the unit cells of the silicon-oxygen tetrahedron and the aluminum-hydroxyl octahedron which are bonded together by electrostatic forces and form the tetrahedral silica sheet or chain and the Gibbsite sheet respectively.

X-ray diagrams of clays show two separate series of lines (or bands), one due to the "two dimensional crystallites" (indices h , k , l), the other a single series of orders, indexed (0 0 l), due to the intersheet separation. Only the latter series changes in adsorption reactions, and from it the (0 0 l) spacing, and thus the separation of the structural sheets are readily deduced. In adsorptive reactions with these minerals (particularly montmorillonite), molecules of water and ions can penetrate between the structural sheets, thus expanding the whole crystallite structure, a change detectable by x-ray diffraction and thus enabling the study of the expansion characteristics of the clay minerals.

The remarkable activity of montmorillonite in adsorption is no doubt connected with a common peculiarity of its crystalline structure, which is such that regular (two-dimensionally crystalline) sheets are superposed without any regularity (except for constant separation) and are held together by relatively weak forces.

As for the application of x-ray diffraction for the identification of clay minerals, the interpretation of the

data requires the conversion of the lines in the x-ray powder pattern to their corresponding interplanar distance so that Hanawalt's(4) method employing the card file of x-ray diffraction data can be used; or an extended series of standard patterns which are used for direct comparison.

PART III

APPARATUS

APPARATUS

ELECTRODIALYZER. The electrodialyzer used was a standard three-cell BRADFIELD type operating with 110 volts D.C. Each of the three cells is separated from the other by cellophane diaphragms which are impermeable to water but highly permeable to ions. The diaphragms are mounted between U-shaped rubber gaskets which in turn are backed by metal plates. This entire arrangement is clamped together forming a sandwich which encloses the three separate cells. This three-cell arrangement is conveniently mounted on a stand. The two outer compartments are the cathode and anode while the central cell contains the material which is to be electrodialyzed. The cathode is a nickel screen and the anode is a platinum screen both of which are placed inside the cells designated as the cathode and anode cells respectively. A glass tube arrangement is inserted into the cathode and anode cells and tap water is run through it continuously such that adequate cooling of the poles is affected.

The sample, mixed with distilled water to form a sol, is placed into the central cell. The outer cells are filled with distilled water which is continuously replaced in the cathode cell from a source located above the equipment, the water being fed by gravity flow and maintained

at a constant level within the cell by a simple overflow arrangement. The anode is periodically replenished with distilled water by manual draining and refilling, only periodic replacement of the distilled water being necessary since the anion content of clays is slight compared to the cation content.

This BRADFIELD electrodialyzer was manufactured by the Central Scientific Co. (Cenco) and the wiring diagram is as shown in Figure 3.

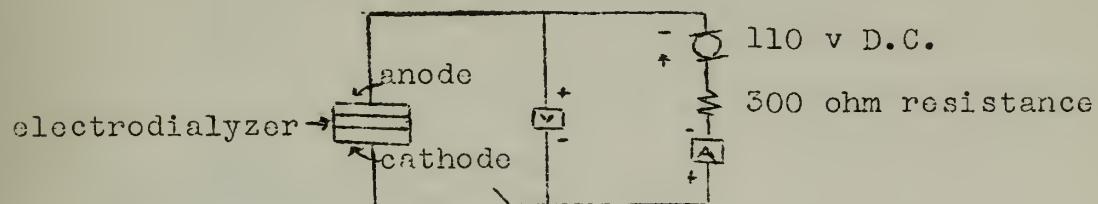


Figure 3. Wiring diagram of the BRADFIELD three-cell electrodialyzer.

The theory of electrodialysis of clays will not be attempted here as there are many fine references pertaining to this, one of which is exceptionally good⁽⁵⁾.

Figure A (page 82, Appendix) is a photograph of the assembly used for the electrodialysis of the Rock River, Wyoming Bentonite.

APPARATUS FOR THE IONIC SATURATION OF HYDROGEN BENTONITE. This apparatus merely consisted of a 600 ml beaker containing the hydrogen bentonite as received from the electrodialyzer, a mechanical stirrer employing a glass stirring rod, a 50 ml burette containing the appropriate

hydroxide compound, and a BECKMAN pH meter Model G with calomel electrodes. The clay, still in sol form, was beat with the stirrer while the hydroxide compound was slowly added. The calomel electrodes of the pH meter were kept immersed in the sol thus enabling a constant recording of the pH of the material.

SAMPLE EXTRUDER. This extruding device is best illustrated by Figure 4. The dry powdered clay is mixed with

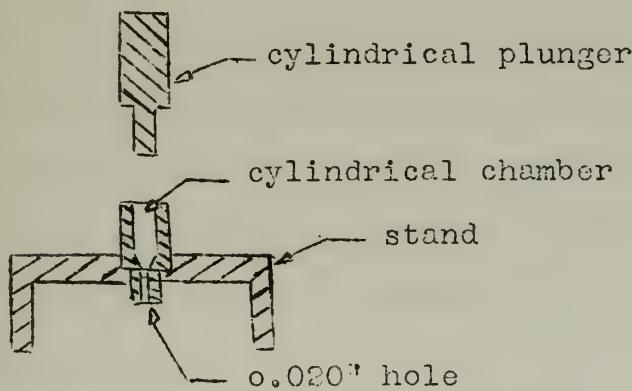


Figure. 4. Sample Extruder.

a suitable binder, Duco Household Cement, and is packed into the cylindrical chamber. The turned down portion of the cylindrical plunger, which fits into the chamber with extremely close tolerance, is used to compress the clay in the chamber thus forcing it to be extruded through the 0.020" hole producing a thread-like clay sample 0.020" in diameter. The stand is used to support the complete assembly. High grade steel was used in the production of each piece of this extruder. A photograph of this complete assembly is shown in figure A (page 81 , Appendix).

X-RAY EQUIPMENT. The general set up for taking X-ray diffraction patterns of clays is illustrated in Figure 5.

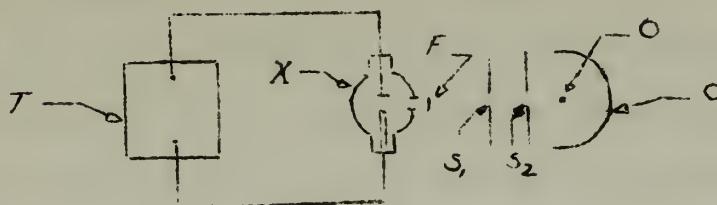


Figure 5. Schematic diagram illustrating general set-up for the X-ray diffraction of clays.

T is a current transformer, X is an x-ray tube, F is a filter, S₁ and S₂ are slits in thin sheets of lead, O is the mounted clay powder sample and C is a narrow strip of photographic film bent over a semi-circular strip of brass concentric with the clay sample. This diagram is highly simplified to better illustrate the fundamental considerations involved.

The filter is a sheet of metal chosen of such material that it specially absorbs all wave lengths shorter than the desired one, leaving practically nothing but a single intense line, the α line of the K series of the anode material. For a copper target, the proper filter is nickel. X-rays first pass through the filter which absorbs all but a single wave length; then through the two slits which confine them to a narrow beam (about 1 mm wide); then through the powdered clay sample which scatters or "reflects" a very small fraction of them; and thence to the center of the photographic film (which can be a flat film as well as a cylindrical strip of film). When the film is developed it shows,

in addition to the over-exposed portion in the center where the direct beam strikes, a series of other lines on each side of the center. These lines constitute the diffraction pattern of the clay sample (see previous section on THEORY).

An x-ray tube with a copper target and a nickel filter were chosen for the work in this thesis as the α line of the K series of this material gives maximum sample penetration with minimum exposure (three hours).

No x-ray theory nor wiring diagrams for the particular x-ray used in this thesis will be given as they are quite involved and are discussed at length in any standard text dealing with x-rays and radiography.

For the General Electric diffraction tube used in this work the maximum kilovoltage is 50 K-v.P. and the maximum tube current is 20 millamps.

A photograph of the x-ray tube is shown in figure B (page 82, Appendix).

POWDER CAMERA. The DEBYE SCHERRER powder camera is widely accepted as an excellent x-ray camera for obtaining x-ray diffraction patterns of powdered samples. A drawing of this powder camera, used in this work, is given in figure 7 (page 83, Appendix) and a photograph of it in position with the x-ray tube is shown in figure (page 82, Appendix). It is essentially a brass cylinder, closed at one end, with a brass collar which fits, with close tolerance, concentrically inside. A strip of x-ray film two inches wide fits against the inside of the cylin-

der and is pressed flat against it by a simple knob and slide arrangement which engages the ends of the film and by sliding along the cylinder's perimeter, forces the film to be flush against it. The collar, which has a slit along its perimeter to allow the passage of x-rays to the film, fits inside the cylinder against the film thus holding the film secure in its position. The slit is covered with opaque paper to protect the film from exposure to light and yet does not hinder the passage of x-rays. The two-slit arrangement as described under the x-ray apparatus section is made possible by a tapered spindle which is inserted through the cylinder, the film, and the collar and projects inwardly training toward the exact center of the cylinder. This spindle has a 0.030" diameter hole drilled through it and thus serves the purpose of narrowing or collimating the x-rays to 0.030" in width. With proper alignment of the camera, the narrowed x-rays are directed toward the sample by the collimation spindle. The camera is mounted on a stand which makes possible the adjustment of the camera about horizontal axes at right angles to each other.

The sample, which must be in the form of a cylinder about 0.2 mm in diameter and one inch long, is mounted in a small sample holding tube which fits inside a well in the center of the camera. The x-rays, reduced to 0.030" width, are directed to the sample by the collimation spindle, pass through the sample being reflected during this

transit, and continue on through another spindle which fits through the cylinder diametrically opposite the collimation spindle. This second spindle plays the role of allowing the x-rays to pass through the entire assembly so that they can be detected on an x-ray-sensitive screen mounted on a small stick which is held in the operator's hand. Proper alignment of the powder camera is accomplished when a concentrated x-ray beam is seen scintillating from the screen.

FLAT CASSETTE. This is nothing more than a metal rectangular frame for holding and mounting, into position before the x-ray tube, 5" x 7" flat, rectangular photographic film. A 5" x 7" piece of opaque paper, which protects the film from exposure to light but does not hinder the passage of x-rays, is placed into the frame and then 5" x 7" flat film is placed inside the frame against the paper. A 5" x 7" piece of stiff cardboard is then placed against the film and everything is finally sandwiched together by a metal backing which is forced against the cardboard by two springs which bear against the frame. This assembly is mounted before the x-ray tube and a 0.020" pinhole arrangement narrows the beams which are directed at the cassette 6 cm. away. A small lead plug suspended by a wire is placed against the cassette where the x-rays strike so as to absorb the direct beam. The sample, again in the form of a small tube or cylinder, is

mounted across the center of the pinhole such that the narrowed x-ray beams pass through it and are reflected onto the film in the cassette giving the desired diffraction rings.

A photograph of the flat cassette in position with the x-ray tube is shown in figure B (page 82, Appendix).

MEASURING DEVICE. This is used to measure the radii of the diffraction rings of the diffraction patterns appearing on the negatives. The film, both strip and rectangular, is clamped in a horizontal position and a slide viewer with a reading hair and vernier is placed with the hair coinciding with the ring being read. The radius of the ring is then computed from the reading on the vernier. The measuring device is placed over a light-box so that the light shining up through the film enhances the reading of the film.

DEVELOPING AND PRINTING EQUIPMENT. Standard developing and printing equipment was used in developing and printing the diffraction patterns.

PART IV

PROCEDURE

PROCEDURE

Rock River, Wyoming Bentonite; Dry Branch, Georgia Kaolinite; and Joliet, Illinois Illite - Bearing Shale were chosen as representative of the three basic clay types.

The cations H^+ , Na^+ , K^+ and Ca^{2+} were selected for the ionic saturation of the clays as they are commonly found in clays in nature.

In order to study the expansion characteristics of the chosen clays due to their hydration, the prepared clay samples were first oven dried at $110^{\circ}C.$ for 24 hours and were then completely saturated with distilled water.

Each clay was passed through a No. 200 mesh sieve in an attempt to arrive at the optimum particle size for sharp x-ray diffraction patterns.

HOMO-IONIC SATURATION OF CLAYS. The Bentonite was placed in a mechanical mixer along with distilled water and was thoroughly mixed producing a clay sol which was placed into the central cell of the Bradfield electrodialyzer. Electrodialysis of this clay sol was allowed to continue until the pH was reduced to 3.2 as compared to the original pH of 7.9. The pH determinations were made with the use of a standard Beckman pH meter. Electrodialyzing a clay sol to a pH of 3.0 to 3.5 produces a pure H^+ clay⁽⁷⁾. The H^+ bentonite sol with a pH of 3.2 was

removed from the electrodialyzer and a portion of it was placed into a 600 ml. beaker. Using the arrangement as described under APPARATUS, the sol was beat continuously while a 0.1 normal solution of sodium hydroxide was slowly added until a constant pH reading of 8.2 was obtained. This method was in accordance with reference (7) for the preparation of a relatively pure sodium clay. Potassium and calcium bentonite were also prepared by this method using 0.1 normal solutions of potassium hydroxide and calcium hydroxide respectively in place of the sodium hydroxide.

The corresponding homo-ionic samples of kaolinite and illite along with more bentonite were prepared by W. D. Ennis and J. C. Hufft⁽⁹⁾, by the potentiometric titration method starting with hydrogen clays which were obtained by displacement with hydrochloric acid.

The following samples were made available for x-ray diffraction studies: H^+ , Na^+ , K^+ and Ca^{++} bentonite using electrodialysis to obtain the H^+ bentonite; H^+ , Na^+ , K^+ and Ca^{++} bentonite, illite, and kaolinite using HCl displacement to get the H^+ clays; and the original or as received samples of bentonite, illite, and kaolinite. X-ray diffraction patterns were taken of each of the above samples in the oven-dry state ($110^{\circ}C.$ for 24 hours) and the completely hydrated state.

PREPARATION OF CLAY SAMPLES FOR X-RAY DIFFRACTION.

After obtaining the prepared clay samples, a suitable method for mounting the samples in the x-ray camera had to be devised. Before the method of mounting the powdered specimen, whether dry or fully hydrated, could be selected, the optimum thickness of the sample to be used had to be determined. An approximation as to the thickness required was arrived at by the substitution of estimated values in the equation⁽⁸⁾ $t = \frac{2}{\mu}$ where t is the optimum thickness and μ is the linear absorption coefficient calculated from the mass absorption coefficient according to the relationship: $\mu = d \sum p \left(\frac{\mu}{\rho} \right)$

$$= d \left[p_A \left(\frac{\mu}{\rho} \right)_A + p_B \left(\frac{\mu}{\rho} \right)_B + p_C \left(\frac{\mu}{\rho} \right)_C \dots \right]$$

d being the density of the material, p the elemental fraction in the compound and $\frac{\mu}{\rho}$ the mass absorption coefficients of the elements for the wave length of the radiation used. As previously mentioned, only an approximation of the optimum thickness was obtained by substitution in this equation as d and p had to be estimated, their actual values being unavailable. This approximate thickness was 0.20 mm. Past researchers had packed their samples into capillary tubes made of glass but this was ruled out because measurements on Pyrex tubes with wall thickness just sufficient to permit careful handling showed forty to fifty percent absorption of the $\text{CuK}\alpha$ radiation. Plastic materials (materials with amorphous patterns and impermeable to moisture) were preferred to

glass and in this respect, polyethylene tubing was first used to make the specimens. The tubing was filled with a clay sample, the ends were sealed by squeezing the plastic with hot tweezers, and the whole was pressed flat to about 0.2 mm. thickness. This proved unsatisfactory as the sample was not the proper shape nor thickness and the resulting pattern was highly diffuse and distorted. The size of the tubing was reduced and tightly packed with some of the dry powdered clay so as to approximate a cylinder about 0.2 mm. in diameter. This improved the sharpness of the pattern but did not remove the distortion due to its not being truly cylindrical. An attempt was then made at rolling the powder between two glass slides using Dupont Duco cement as a binder. The cement also acts as a diluent, and if kept to a minimum, generally does not affect the background of the diffraction pattern. According to Schielitz⁽⁸⁾, "When Dupont household Duco cement is used as a binder for the powdered montmorillonite-type clay samples, the diameter and sharpness of the innermost line in the pattern gives some information concerning the identity of the adsorbed cations. Preliminary observations indicate that a broad diffuse line represents a mixture of cations, whereas a sharp narrow line represents a relatively pure single cation". This method of the two glass slides proved inadequate, however, as it was too difficult to obtain the right size and shape of speci-

men. It was finally decided to try extruding the clay using Duco cement again as a binder and clay conditioner. This, of course, could only be applied to the dry samples. An extruding device (see APPARATUS) was thereupon designed such that the clay could be extruded into a thread-like specimen through a 0.013" diameter hole. This diameter proved to be too small requiring a long exposure time and the hole was increased in diameter to 0.020". This proved to be highly satisfactory as the dry clay, mixed with a minimum amount of cement, was quickly and easily extruded; the resulting specimen had the proper cylindrical shape, the right thickness and the right consistency such that the resulting patterns were sharp, complete and uniform. The specimen also proved to be durable, withstanding a great deal of handling without breaking and could be easily reclaimed and filed away for future reference and use. A minimum amount of sample (less than 0.01 gram) produced several specimens two inches in length. All the final dry specimens were prepared for the x-ray by this extrusion method.

The preparation of saturated clay samples for x-ray diffraction proved to be a more perplexing problem. Naturally, extrusion was out of the question. Other investigators had packed clay pastes into glass tubing of various diameters sealing them with a waterproof cement such as DeKhotensky cement or plastocene in order that no

moisture be lost during x-raying. As previously mentioned, glass has high x-ray absorption and also has a halo-like diffraction pattern with long exposures. The use of plastic materials was the natural recourse and polyethylene having failed, it was decided to attempt the making of smaller, rigid plastic tubing by coating an annealed copper wire of the desired size with a plastic solution and removing the formed tubing after the solution had dried. Polyethylene, Polystyrene, Lucite and Duco cement were each dissolved and formed on a wire, but each proved too difficult to remove from the wire when dried. Success was finally achieved using ethyl cellulose dissolved in methyl ethyl ketone and xylol⁽¹⁰⁾. The annealed copper wire was straightened by a minimum amount of stretching and was cut into two inch lengths. The dissolved plastic was applied to the wires and allowed to dry in an oven at 50°C. for 48 hours. After removal from the oven, the coated wires were gently stretched thus breaking the bond between the plastic and wire permitting the removal of the tubes. Drying the plastic-coated wires for periods in excess of 48 hours resulted in the development of a stronger bond between the plastic and wire, making the removal of the plastic tube too difficult. It should also be noted that if the wire is stretched too much while being straightened, ductility is sacrificed and the wire breaks while being drawn to permit removal of the

tubing.

A photograph of the tubes is shown in Figure B , p. 81, Appendix.

The tubes made in this manner were cylindrical, the right size and rigid such that they could easily be handled. They were filled by inserting one end into the hydrated clay sample and running the wire, on which the tubes were formed, through the tubes into the sample. The wire was then pulled through in the opposite direction and thus created a vacuum such that the clay paste was drawn into position in the tubes. Possible leakage of tubes was checked by drawing the clay paste inside and then pushing it out again to see if any escape of the clay took place through the tube walls. Having been filled with the hydrated samples, the tubes were sealed by pinching the ends with hot tweezers or by dipping the ends into the dissolved plastic and allowing the plastic to dry. Unfortunately, neither method was thoroughly effective as the samples dried out after 6 or 8 hours thus necessitating immediate x-raying after the filling of the tubes. A more effective means of sealing the tubes is yet to be found.

The first tubes made in this manner were formed on No. 36 B& S gauge wire resulting in a tube diameter of 0.127 mm. These tubes proved to be too small requiring excessive exposure times and No. 24 B&S gauge wire was then used giving a tube diameter of 0.5 mm. This proved

to be ideal as the patterns of the hydrated samples contained in these tubes were complete, sharp and uniform requiring only three hours exposure, the same amount of time as was required with the final extruded dry specimens.

It should be noted at this point that the hydrated samples were obtained by beating the homo-ionic saturated clays and the as received clays in a mechanical beater with excessive amounts of distilled water for fifteen to twenty minutes after which they were allowed to stand until placed into the tubes for x-raying.

The dry samples were prepared by drying the treated clays and the as received clays, grinding them with mortar and pestle, passing them through a No. 200 mesh sieve and drying them in an oven at 110°C. for 24 hours. Those particle sizes passing the No. 200 mesh sieve proved to be ideal for sharp, clear diffraction patterns.

PROCEDURE FOR OBTAINING THE DIFFRACTION PATTERNS.

The x-ray specimens of the dry and hydrated samples were secured in the sample holder of the Debye Sherrer Powder Camera (see APPARATUS), the camera was properly aligned and a three hour exposure was allowed. Kodak type ^K_A x-ray film was used in the camera as it gives the best contrast for such work at a higher relative speed. The α line of the K series of Copper was used as the radiation as it gives maximum penetration with a minimum exposure.

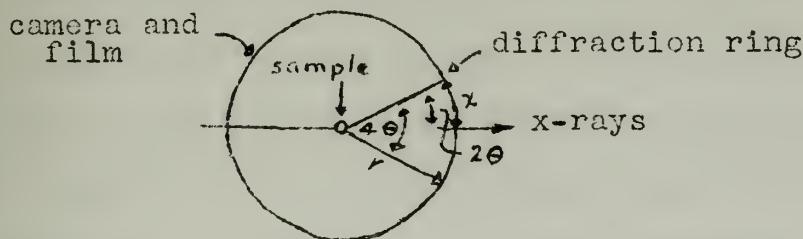
The Debye Sherrer Camera proved inadequate for taking

diffraction patterns of the bentonite samples as the innermost ring occurred in that region on the film where the hole for the spindle, opposite the collimation spindle, was punched. In attempting to correct for this, the α line of the K series for Chromium radiation was used as the wavelength is about twice that of the corresponding copper radiation and thus would increase the diameter of the innermost ring; however, this also proved inadequate. A flat cassette involving flat film which did not have to be punched with holes was then used with satisfactory results. The same was feared for the illite patterns so the cassette was used for five of them until it was discovered that there was no inner ring for this pattern, whereupon the powder camera was used. The lattice spacing of kaolinite is such that the powder camera was ideal for kaolinite patterns. Refer to the discussion for the flat cassette in Part III (APPARATUS).

Standard darkroom procedure was followed in developing the resulting diffraction patterns. A developing tank was provided with the proper developing solution, wash water and fixing solution. The film was left in the developing solution for seven minutes, washed for one minute, fixed for twenty minutes and finally washed for thirty minutes after which it was allowed to dry.

READING THE PATTERN AND COMPUTING THE d -SPACING. The radii of all visible rings on the patterns were read from

the negatives using the measuring instrument described under APPARATUS and the d-spacings of the rings were computed. These rings represent the various families of planes in the respective clay crystals with the innermost rings for bentonite and kaolinite clays representing the basal, net or dool plane (see THEORY). The illite clays had no inner ring (see RESULTS AND CONCLUSIONS). The method of computation for the d-spacings for the patterns obtained using the powder camera is as follows:



$$\frac{2\pi r}{360} = \frac{\chi}{2\theta}$$

$$2\theta = \frac{360\chi}{2\pi r}$$

$$\theta = \frac{90\chi}{\pi r}$$

Bragg's law: $n\lambda = 2d \sin \theta$

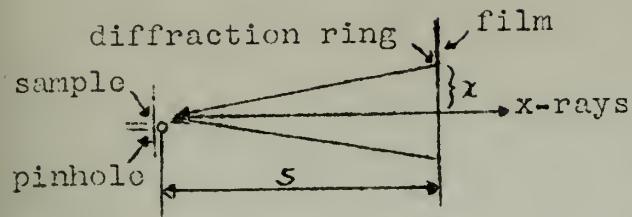
$$d = \frac{n\lambda}{2\sin\theta}$$

Substitute for θ :

$$d = \frac{n\lambda}{2\sin\left(\frac{90\chi}{\pi r}\right)}$$

wherein $n=1$, $r=5.7$ cm., χ is measured in cm. with vernier, $\lambda = 1.54\text{\AA}^\circ$ for $\text{CuK}\alpha$ radiation, and d is the computed spacing in \AA° .

For the flat cassette:



$\tan 2\theta = \frac{x}{s}$ where x and s are measured and θ is computed.

$d = \frac{n \lambda}{2 \sin \theta}$ where $n = 1$,

$\lambda = 1.54\text{\AA}^\circ$ and d is the computed spacing in \AA° .

METHOD FOR IDENTIFICATION OF CLAYS. The d -spacings for all visible rings are computed and recorded along with the relative intensity of each ring as determined by eye, the most intense having a relative intensity of the order 1, the second most intense having an order of relative intensity of 2, etc. These computed and recorded d -spacings and orders of relative intensity are then compared directly with that A.S.T.M. INDEX CARD which matches most closely (see page 42, APPENDIX). This method of identification using A.S.T.M. Index Cards is known as the HANAWALT method⁽⁸⁾.

The other method of identification is simply direct comparison of the pattern of the unknown with other patterns of similar materials, and by direct matching or similarity of patterns, the unknown is identified. See RESULTS AND CONCLUSIONS for further discussion of identification procedures.

POSITIVE PRINTS OF PATTERNS. Positive prints of all diffraction patterns were made on glossy printing paper following the standard procedure for printing.

PART V

RESULTS AND CONCLUSIONS

RESULTS AND CONCLUSIONS

The clay particle size passing a No. 200 mesh sieve and retained on a No. 325 mesh sieve proved to be the optimum particle size for obtaining sharp and complete x-ray diffraction patterns. Those particle sizes not passing a No. 200 mesh sieve were too large giving "Laue spots"⁽³⁾, scattered spots, which disfigured the patterns (see the pattern for the dry, as received bentonite). Particle sizes much smaller than those passing a No. 325 mesh sieve were too small requiring excessive times of exposure and giving patterns which were diffuse.

Use of the extruding device, with Duco cement as a binder, producing thread-like samples 0.020" in diameter was successful in that the specimens were the proper shape, size and consistency giving the sharp, complete patterns which appear in the APPENDIX. (See APPENDIX for prints of all patterns).

The inadequacy of the use of polyethylene tubing and of rolling the sample between glass slides is illustrated by the respective patterns.

Ethyl cellulose tubing formed on copper wire 0.5 mm. in diameter was the solution for mounting the hydrated samples. Sharp, clear and undistorted patterns resulted from this method. Difficulty was experienced in effectively

sealing the tubes and slight loss of moisture occurred making it impossible to retain the samples in their originally hydrated state. Dehydration occurred at a rate too slow to affect the diffraction patterns.

The methods used for preparing both the dry and hydrated samples are simple and quick and produce specimens which are easy to handle.

The α line of the K series of copper radiation gave maximum sample penetration with minimum exposure.

The Debyo Sherrer powder camera, 5.7 cm. in diameter, was satisfactory for kaolinite and illite diffraction patterns. The large basal plane spacing occurring in the bentonite could not be recorded using the powder camera making necessary the use of the flat cassette discussed under APPARATUS.

Of the x-ray films available, Kodak Industrial x-ray film Type K is the best for x-ray diffraction of clays as it gives the maximum contrast with the highest relative speed.

The interpretation of the diffraction patterns was limited to the analysis of interplanar spacings only (see pages 36 and 37 for a complete tabulation of these spacings). No attempt at crystal analysis was made as it requires extensive knowledge and experience in crystallography.

In agreement with the theory of the activity of ben-

tonite in adsorption reactions with various cations and with water, the diffraction patterns of the Rock River, Wyoming bentonite showed a marked change in the basal plane spacing. The change in spacing varied in accordance with the nature of the adsorbed ion, or ions, and with the degree of hydration. A comparison of the basal plane spacings of the bentonite prepared by electrodialysis and titration is as follows:

Oven-dry: H > Ca > Na > K

Fully hydrated: H > Na > K ≈ Ca

Net change (swelling): $\text{Na} > \text{K} > \text{Ca} > \text{H}$

For the bentonite prepared by HCl displacement and potentiometric titration:

Oven-dry: K > H > Ca > Na

Fully hydrated: $H > Ca$ K and Na were not obtainable for reasons which are explained below.

Barshad⁽¹²⁾ obtained the following results for bentonites of different origins:

Oven-dry (time and temperature unknown): Ca > H > K > Na

Hydrated (immersed in water): $\text{Na} > \text{H} > \text{Ca} > \text{K}$

Net change (swelling): $\text{Na} > \text{H} > \text{Ca} > \text{K}$

The differences in the above results are believed due to:

(1) different methods used in preparation of samples with subsequent difference in quality of samples, and (2) unlike degrees of hydration and dehydration. In strict accordance with the crystal radii and the hydrated radii of the cations

involved, the order of basal plane spacing should be:

Dry: Ca>K>Na (?H)

Hydrated: Na>K>Ca (?H)

Three reasons why this order of spacing was not obtained are:

- (1) The methods used for the preparation of the samples are open to question as no positive means of sample analysis was undertaken, i.e., it was not known if the clays were truly homo-ionic.
- (2) It is doubtful if the complete dehydration of a clay can be accomplished without destroying the lattice structure and if dehydrated ions can exist within the clay.
- (3) Drying homo-ionic clays under the same conditions does not mean that each has the same moisture content.

The innermost ring of a montmorillonite type clay is an indication of the nature of the adsorbed ion and the extent to which the clay has completed its reaction with water. A sharp ring denotes that the clay is principally saturated with only one ion whereas a broad, diffuse ring indicates saturation with a mixture of ions. (See bentonite patterns, pages 57 and 59). With a complete set of standards including such information as the origin of the clay, method of preparation, and condition of moisture, it would be possible to more nearly establish the identity of the adsorbed ion of a homo-ionic clay by comparison of basal plane spacings. This could not be applied to clays

saturated with ions which have the same valence and hydrated and dehydrated radii such as Ca^{++} and Mg^{++} .

Since such standards are not presently available, x-ray diffraction cannot be used to establish definitely the identity of the adsorbed ion or ions.

If the reaction between bentonite and water has not reached completion, i.e., the clay is in the process of adsorbing water into its lattice structure, the innermost ring appears broad and diffuse.

Due to the similarity in the d_{001} spacings of the bentonite samples x-rayed, it is believed that they were all predominantly hydrogen bentonites with varying degrees of the hydrogen ion replaced by the other respective ions. The Na^+ , K^+ and Ca^{++} bentonites had basal plane spacings which corresponded more nearly to the spacing for the hydrogen bentonite than to the spacings as established by other investigators^{(6)(8)and(12)} for bentonite saturated with the other ions.

The interplanar spacings of kaolinite remained constant showing that the lattice structure of kaolinite is such that ions and molecules of water are adsorbed on the surface of this clay rather than within the structure itself.

The illite sample used had no inner ring indicating that insufficient illite was present in the materials. By direct comparison of the diffraction pattern of this material, it was found to be similar to the pattern for an

illite-glaucite shale as found in reference (8).

The Hanawalt method for the identification of clays from their diffraction patterns involves the use of A.S.T.M. card indices wherein the interplanar spacings and relative orders of intensity of the unknown are compared with those appearing on the index cards. This method is illustrated in figures B and B , pages 42 and 60 , but is of limited value as the number of index cards for clay minerals is insufficient and the cards lack such necessary information as the origin of the clay, condition of moisture, and ion content.

The method of direct comparison of patterns of unknowns with patterns of known materials is a quick and easy method of determining the type of clay mineral. Excellent patterns of known clay minerals which could be used for direct comparison are shown in figure 6 , page 80 .

The possible sources of error in the x-ray analysis of clays in this thesis are:

- (1) Uncontrolled moisture, both dry and hydrated.
- (2) Microscopic irregularities in shape of specimen which may create slight distortions.
- (3) Possible film shrinkage - considered negligible due to careful developing.
- (4) Sample, when mounted in the powder camera, may deviate from a vertical straight line thus offering possible source of distortion.

(5) Errors involved in measuring distance from center of sample to surface of film in flat cassette.

(6) Human errors involved with use of measuring device for radii of diffraction rings.

X-ray diffraction is of inestimable value for the study of clay minerals for the following reasons⁽⁸⁾:

- (a) The technique required to make x-ray patterns is relatively simple.
- (b) Since this method is indestructive, the sample can be used for further studies by other methods.
- (c) Only a very small amount (less than 0.01 of a gram) of the material is needed to make up a sample.
- (d) Only a limited accuracy in measurements is necessary when making a qualitative analysis.
- (e) A file of diffraction patterns constitutes a permanent record.

It must be noted, however, that x-ray diffraction is not a panacea for all problems and its utility is usually considerably enhanced if it is used in connection with other methods, especially differential thermal, chemical, and spectrographic analyses. This is particularly true for the investigation of complex mixtures because at the present time, an appreciable amount of a constituent, from one to thirty percent⁽¹³⁾, must be present in a mixture before its presence can be detected. Use of improved techniques should do much to correct this situation⁽⁸⁾.

BENTONITE INTERPLAAR SPACINGS (\AA°)

Electrodialyzed and Titrated

		Innermost \downarrow										Outermost \uparrow			
As received Bent.	Oven Dry	15.38	5.00	4.50	---	3.93	---	3.74	3.36	3.25	---	2.56	---	1.82	---
H - Bentonite	Hydrated	---	4.96	4.50	4.07	3.74	3.36	3.36	3.36	3.36	3.36	2.86	2.56	2.12	1.81
	Oven Dry	15.39	20.30	4.51	4.51	4.51	4.51	4.51	4.51	4.51	4.51	2.57	2.57	2.57	2.57
Ca- Bentonite	Hydrated	15.59	19.27	4.47	4.47	4.47	4.47	4.47	4.47	4.47	4.47	2.58	2.58	2.58	2.58
Na- Bentonite	Hydrated	13.25	19.45	4.46	4.46	4.46	4.46	4.46	4.46	4.46	4.46	2.84	2.84	2.84	2.84
K - Bentonite	Hydrated	13.14	19.27	4.45	4.48	4.48	4.48	4.48	4.48	4.48	4.48	3.25	3.25	3.25	3.25

HCl Displaced and Potentiometric Titrated

H - Bentonite	Oven Dry	15.70	---	4.46	---	---	---	3.34	---	---	---	2.56	---	1.82	---
	Hydrated	20.30	---	4.52	---	---	---	3.37	---	---	---	2.59	---	2.59	---
Ca- Bentonite	Oven Dry	13.62	---	4.46	4.24	---	---	3.33	---	---	---	2.56	2.44	2.44	1.81
	Hydrated	19.03	5.12	---	---	---	---	3.34	---	---	---	2.56	2.56	2.56	2.56
Na-Bentonite	Oven Dry	13.49	4.94	4.44	4.44	4.44	4.44	3.69	3.53	3.19	---	2.56	2.56	2.56	1.81
K - Bentonite	Hydrated	13.89	4.95	4.44	4.44	4.44	4.00	3.58	3.58	3.58	3.58	2.82	2.82	2.82	2.34
	Oven Dry	13.89	4.95	4.46	4.46	4.46	4.46	3.71	3.55	3.55	3.55	2.55	2.55	2.55	1.84
	Hydrated	---	4.83	---	---	---	---	3.59	3.59	3.59	3.59	2.72	2.72	2.72	2.21

KAOLINITE INTERPLATELAR SPACINGS (\AA°)

-37-

Innermost Ring \leftrightarrow Outermost

		Innermost Ring												
As received	Kaolin	7.18	--	4.18	3.61	2.58	2.51	2.35	--	2.00	--	--	1.49	
	Dry	7.13	4.41	4.17	3.57	2.56	2.34	2.30	1.98	--	1.66	1.49		
	Hydrated	7.21	--	4.18	3.59	2.58	2.51	2.33	2.32	--	--	--	1.49	
	Oven	Dry	7.13	4.42	4.19	3.58	2.57	2.50	2.35	2.30	1.99	--	1.67	1.49
	Hydrated	7.21	4.43	4.18	3.58	2.57	2.50	2.34	2.30	2.04	--	1.67	1.49	
	Oven	Dry	7.15	4.41	4.19	3.56	2.57	2.50	2.34	2.30	1.99	1.79	1.67	1.49
	Hydrated	7.13	4.37	4.13	3.54	2.54	2.48	2.32	2.28	1.93	1.77	1.65	1.48	
	Oven	Dry	7.15	4.42	4.23	3.58	2.56	2.50	2.34	2.30	--	--	--	1.49
	Hydrated	7.15	--	4.23	3.53	--	--	2.33	--	--	--	--	--	1.49
	Oven	Dry	7.15	4.06	4.17	3.55	2.55	2.49	2.33	2.28	1.98	--	--	1.48
	Hydrated	7.13	4.32	4.17	3.55	2.55	2.49	2.33	2.28	1.98	--	--	--	1.48

ILLITIC SHALE INTERPLATELAR SPACINGS

		Innermost Ring											
As received	Ill.	4.43	4.22	3.66	3.30	--	--	2.48	2.14	--	1.80	1.53	1.49
	Dry	5.03	4.51	4.28	5.72	3.36	--	2.48	2.14	2.00	1.82	--	--
	Hydrated	--	4.42	4.31	3.75	3.38	--	--	2.47	2.13	1.99	1.81	1.55
	Oven	Dry	--	4.50	4.26	--	3.36	2.53	2.47	2.13	1.99	1.82	1.54
	Hydrated	--	--	4.50	4.29	--	3.36	2.59	2.47	2.14	1.99	1.84	--
	Oven	Dry	5.06	4.54	4.32	3.75	3.39	2.60	2.46	2.14	1.99	1.82	--
	Hydrated	--	--	4.45	4.24	--	--	2.56	--	--	--	1.80	1.53
	Oven	Dry	--	4.52	4.31	--	3.36	2.59	2.48	2.14	1.99	1.82	--
	Hydrated	--	--	4.55	4.34	3.75	3.38	2.60	2.48	2.14	1.99	1.82	--
	Oven	Dry	5.03	4.55	4.26	--	3.28	2.58	2.48	2.14	1.99	1.82	--
	Hydrated	--	--	4.51	4.26	--	--	2.45	2.12	1.98	1.81	1.53	1.50

PART VI

RECOMMENDATIONS

RECOMMENDATIONS

In order to fully utilize the method of x-ray diffraction for the analysis of clay minerals, it is important that a complete file of standard diffraction patterns be established for all the natural minerals under the montmorillonite, illite, and kaolinite groups of basic clay minerals. Each of the minerals constituting the file of standard patterns should be x-rayed in its natural state. Also the bentonites and illites should be carefully treated such that each is purely saturated with single types of cations in the Hoffmeister series. They can then be x-rayed producing complete, clear and uniform diffraction patterns forming a necessary part of the file of standard patterns. Further work should also be done in carefully treating these clays such that varying percentages of different ions are adsorbed within their lattices. It is fully realized that such work would be extremely difficult, but at the same time, it is considered necessary for a complete file. Included with each of the above patterns should be the following important information: origin of clay, method used for ionic saturation, quantitative and qualitative analysis of clay, condition of moisture giving percent hydration, and tabulated interplanar spacings and orders of relative intensities. Such information could be obtained and checked by the advantageous use of other methods of clay analysis including

spectroscopic studies, differential thermal analysis, optical analysis, dehydration curves, and quantitative and qualitative chemical analysis. Several of the foregoing methods of analysis should always be used in conjunction with x-ray analysis of clays. With a complete set of standard patterns as outlined above, x-ray analysis would be a quick, accurate and easy method for determining the type of clay, structural classification, nature of adsorbed ion and positive identification. Without the prescribed information which should be included with each pattern, the file of patterns would be relatively worthless.

An interesting and valuable study would be that of determining the swelling characteristics in detail of expanding lattice-type clays by carefully controlled methods for successive degrees of hydration, using x-ray diffractions to detect and record the progress of swelling of the clay from its "dry" state to its completely hydrated state. This could serve as an informative insight as to the nature of the swelling of clays due to hydration.

Associations of montmorillonite with organic materials have been studied from time to time and it is recommended that further research be conducted in this field as it has already resulted in important discoveries relating to more accurate and detailed analyses of clays by x-ray diffraction⁽¹⁵⁾.

The technique of x-ray diffractions as developed in this thesis is considered highly satisfactory and easy to

duplicate; however, it is recommended that future investigators in this work devise a more effective method for sealing the small plastic tubes so that no escape of moisture will occur from the hydrated clay samples. Such future investigators should also become more familiar with the science of crystallography thereby putting themselves in a more advantageous position to extract information, in addition to what was brought out in this thesis, from the diffraction patterns.

Calibration of the powder camera using a known standard such as NaCl and the use of equivalent radii for the calculations of d-spacings recorded on flat cassettes are recommended for the elimination of any possible sources of error due to a non-vertical sample mounted in the powder camera and due to inaccuracies involved in measuring the distance from the center of the sample to the surface of the film in a flat cassette.

PART VII

APPENDIX

Figure A. Bentonite pattern obtained by use of polyethylene tubing mounted in powder camera. Note irregularity and diffuseness of pattern. No inner ring appears on right side in area of hole.



Figure B. Bentonite pattern using extruded dry sample mounted in powder camera. Note improvement over figure A in sharpness and uniformity of diffraction rings. No inner ring appears in area of hole.



Figure C. Bentonite pattern using glass slides to roll powdered sample mixed with Ducc cement. Note irregularity and diffuseness of pattern.



Figure D. Bentonite pattern using the α line of the K series of Chromium radiation. No inner ring appears in area of hole.



TYPICAL DIFFRACTION PATTERN OF BENTONITE

A. Rock River, Wyoming Bentonite: As received and oven dried at 110°C for 24 hours.

Ring No.	Radius in cm.	Order of Intensity	Interplanar Distance (Å°)
1	0.695	1	13.38
2	1.915	4	5.00
3	2.145	2	4.50
4	2.645	6	3.74
5	2.985	3	3.36
6	3.105	5	3.25
7	4.92	7	2.28
8	7.165	8	1.82
9	--		
10	--		
11	--		
12	--		

d	12.24	4.48	3.14	1.498	d in Å° $\lambda = .708$	I/I ₁	d in Å° $\lambda = .708$	I/I ₁
I/I ₁	1.000	0.500	0.20	12.20	1.00			
				4.48	0.50			
I	40	20	8	3.14	0.20			
				2.56	0.15			
Bentonite				1.68	0.05			
Z =				1.288	0.03			
A ₀ = b ₀ = c ₀ =				1.250	0.03			
A = C =								
D =								
n = w = e =								

B. A.S.T.M. Index Card for Bentonite

Remarks: Origin, adsorbed ions and moisture content of A.S.T.M. Bentonite unknown.



Ring No.	Radius in cm.	Order of Intensity	Interplanar Distance (A°)
1	-		
2	-		
3	2.155	1	4.50
4	2.495	2	3.93
5	-		
6	-		
7	-		
8	-		
9	4.19	3	2.56
10	-		
11	-		
12	-		

Clay Type: BENTONITE

Adsorbed Ion: As-received

Remarks: Fully Hydrated



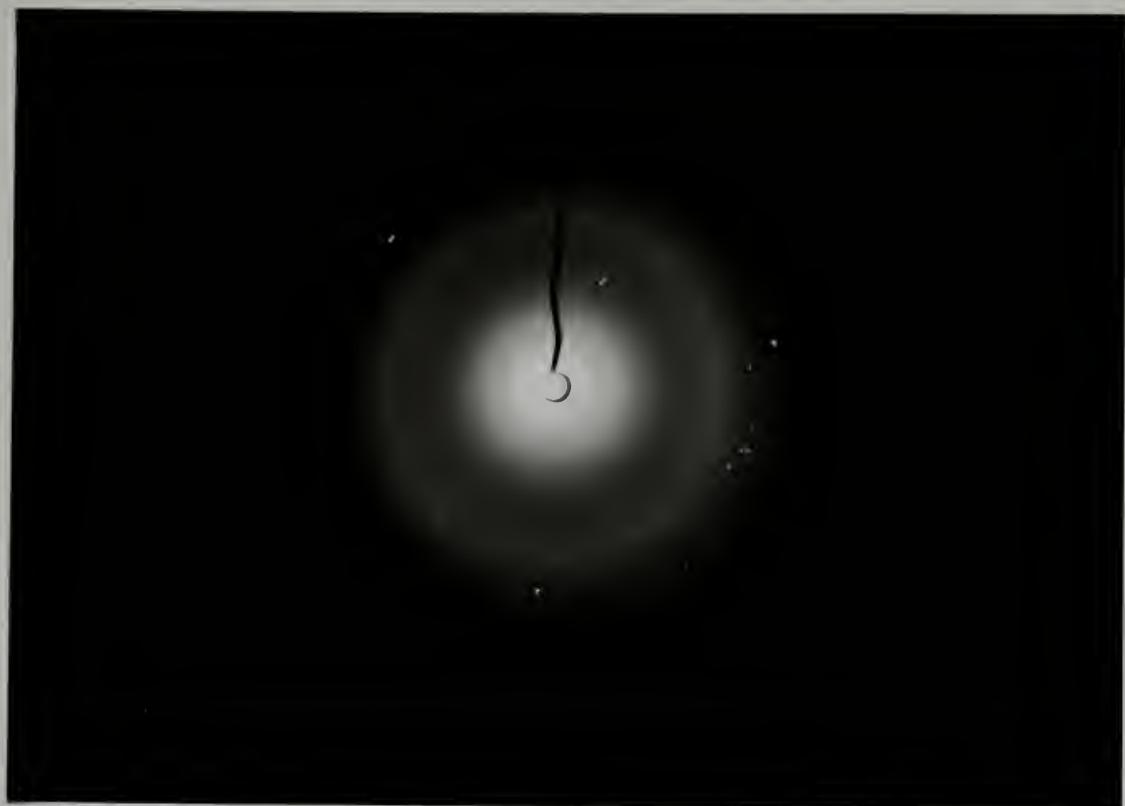


Ring No.	Radius in cm.	Order of Intensity	Interplanar Distance (A°)
1	0.60	1	15.39
2	1.93	5	4.96
3	2.155	2	4.50
4	2.39	6	4.07
5	2.645	4	3.74
6	2.995	3	3.36
7	-	-	
8	3.65	-	2.86
9	4.19	8	2.56
10	-	-	
11	5.5	-	2.12
12	7.2	7	1.81

Clay Type: BENTONITE

Adsorbed Ion: H

Remarks: Electrodialyzed, Fe Oven-dry



Ring No.	Radius in cm.	Order of Intensity	Interplanar Distance (A°)
1	0.455	1	20.3
2	-		
3	2.14	2	4.51
4	-		
5	-		
6	2.99	3	3.36
7	-		
8	-		
9	4.18	4	2.57
10	-		
11	-		
12	-		

Clay Type: BENTONITE

Adsorbed Ion: H

Remarks: Electrodialyzed, Fully Hydrated



Ring No.	Radius in cm.	Order of Intensity	Interplanar Distance (A°)
1	0.67	1	13.89
2	-		
3	2.14	2	4.51
4	-		
5	-		
6	3.04	4	3.32
7	-		
8	-		
9	4.17	3	2.58
10	-		
11	-		
12	-		

Clay Type: BENTONITE

Adsorbed Ion: Ca

Remarks: Electrodialyzed, Oven-dry



Ring No.	Radius in cm.	Order of Intensity	Interplanar Distance (A°)
1	0.48	1	19.27
2	-		
3	2.165	2	4.47
4	-		
5	-		
6	3.03	3	3.33
7	-		
8	--		
9	4.22	4	2.56
10	-		
11	-		
12	-		

Clay Type: BENTONITE

Adsorbed Ion: Ca

Remarks: Electrodialyzed, Fully Hydrated

Ring No.	Radius in cm.	Order of Intensity	Interplanar Distance (A°)
1	0.70	1	13.25
2	-		
3	2.17	2	4.46
4	-		
5	-		
6	3.00	3	3.35
7	-		
8	3.66	5	2.84
9	4.22	4	2.55
10	-		
11	-		
12	-		

Clay Type: BENTONITE

Adsorbed Ion: Na

Remarks: Electrodialyzed, Oven-dry



Ring No.	Radius in cm.	Order of Intensity	Interplanar Distance (A°)
1	0.472	1	19.45
2	-		
3	2.17	2	4.46
4	-		
5	-		
6	3.02	3	3.34
7	-		
8	-		
9	4.19	4	2.56
10	-		
11	-		
12	-		

Clay Type: BENTONITE

Adsorbed Ion: Na

Remarks: Electrodialyzed, Fully Hydrated



Ring No.	Radius in cm.	Order of Intensity	Interplanar Distance (\AA°)
1	0.702	1	13.114
2	-		
3	2.178	2	4.45
4	-		
5	-		
6	--		
7	3.11	4	3.25
8	-		
9	4.203	3	2.56
10	--		
11	-		
12	-		

Clay Type: BENTONITE

Adsorbed Ion: K

Remarks: Electrodialyzed, Oven-dry



Ring No.	Radius in cm.	Order of Intensity	Interplanar Distance (A°)
1	0.48	1	19.27
2	-		
3	2.16	2	4.48
4	-		
5	-		
6	-		
7	-		
8	-		
9	4.2	3	2.56
10	-		
11	-		
12	-		

Clay Type: BENTONITE

Adsorbed Ion: K

Remarks: Electrodialyzed, Fully Hydrated



Ring No.	Radius in cm.	Order of Intensity	Interplanar Distance (\AA°)
1	0.672	1	13.79
2	-		
3	2.16	2	4.48
4	-		
5	-		
6	3.01	3	3.34
7	-		
8	-		
9	4.21	4	2.56
10	-		
11	-		
12	7.2	5	1.82

Clay Type: BENTONITE

Adsorbed Ion: H

Remarks: HCl Displaced, Oven-dry



Ring No.	Radius in cm.	Order of Intensity	Interplanar Distance (\AA°)
1	0.455	1	20.3
2	-		
3	2.14	2	4.52
4	-		
5	-		
6	2.96	3	3.37
7	-		
8	-		
9	4.14	4	2.59
10	-		
11	-		
12	-		

Clay Type: BENTONITE

Adsorbed Ion: H

Remarks: HCl Displacement, Fully Hydrated



Ring No.	Radius in cm.	Order of Intensity	Interplanar Distance (A°)
1	0.682	1	13.62
2	-		
3	2.17	3	4.46
4	2.295	4	4.24
5	-		
6	3.025	2	3.32
7	-		
8	-		
9	4.22	5	2.56
10	4.485	7	2.44
11	4.98	8	2.26
12	7.24	6	1.81

Clay Type: BENTONITE

Adsorbed Ion: Ca

Remarks: HCl Displacement, Oven-dry



Ring No.	Radius in cm.	Order of Intensity	Interplanar Distance (A°)
1	0.485	1	19.03
2	2.165	2	5.12
3	-		
4	-		
5	-		
6	3.013	3	3.34
7	-		
8	-		
9	4.21	4	2.56
10	-		
11	-		
12	-		

Clay Type: BENTONITE

Adsorbed Ion: Ca

Remarks: HCl Displacement, Fully Hydrated



Ring No.	Radius in cm.	Order of Intensity	Interplanar Distance (\AA°)
1	0.70	1	13.49
2	1.94	5	4.94
3	2.16	2	4.44
4	-		
5	2.675	4	3.69
6	3.01	3	3.33
7	-		
8	-		
9	4.22	6	2.56
10	-		
11	-		
12	7.24	7	1.81

Clay Type: BENTONITE

Adsorbed Ion: Na

Remarks: HCl Displacement, Oven-dry



Ring No.	Radius in cm.	Order of Intensity	Interplanar Distance (A°)
1	-		
2	1.94	4	4.94
3	2.175	1	4.44
4	2.45	2	4.00
5	2.78	3	3.58
6	-		
7	3.18	7	3.19
8	-		
9	4.04	9	2.64
10	4.75	6	2.34
11	6.64	8	2.14
12	-		

Clay Type: BENTONITE

Adsorbed Ion: Na

Remarks: HCl Displacement, Fully Hydrated

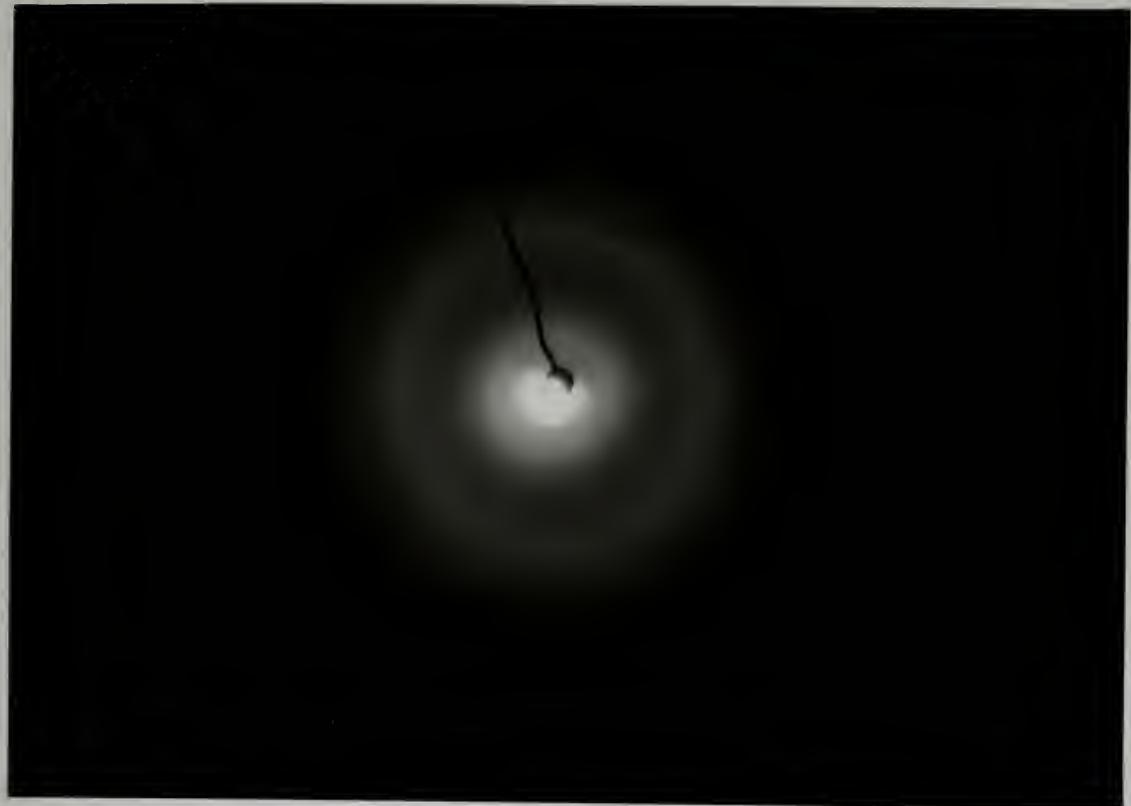


Ring No.	Radius in cm.	Order of Intensity	Interplanar Distance (A°)
1	0.67	1	13.89
2	1.94	4	4.95
3	2.17	2	4.46
4	2.67	6	3.71
5	-		
6	3.01	3	3.35
7	-		
8	3.7	7	2.82
9	4.22	5	2.55
10	-		
11	-		
12	7.14	8	1.84

Clay Type: BENTONITE

Adsorbed Ion: Na K

Remarks: HCl Displacement, Oven-dry



Ring No.	Radius in cm.	Order of Intensity	Interplanar Distance (\AA°)
1	-		
2	1.99	1	4.83
3	-		
4	-		
5	2.77	2	3.59
6	-		
7	-		
8	-		
9	3.89	4	2.72
10	5.17	3	2.21
11	-		
12	-		

Clay Type: BENTONITE

Adsorbed Ion: K

Remarks: HCl Displacement, Fully Hydrated

TYPICAL DIFFRACTION PATTERN OF KAOLINITE

A. Georgia Kaolinite: Saturated with Ca^{++} ion and oven dried at 110°C for 24 hours.

Ring No.	Radius in cm.	Order of Intensity	Interplanar Distance (\AA)
1	1.22	1	7.21
2	1.99	4	4.43
3	2.115	6	4.18
4	2.475	2	3.58
5	2.64	8	3.355
6	3.475	7	2.568
7	3.575	7	2.50
8	3.825	3	2.34
9	3.895	9	2.297
10	4.425	11	2.035
11	5.475	10	1.668
12	6.195	5	1.49

d	3.59	7.24	4.45	d in \AA $\lambda = .708$	I/I ₁	d in \AA $\lambda = .708$	I/I ₁
$\sqrt{I_1}$	1.00	0.80	0.80	7.20	0.80	1.80	0.08
I	12.5	10	10	4.45	0.80	1.67	0.40
				4.30	0.64	1.54	0.16
				4.20	0.48	1.490	0.56
$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$				4.04	0.32	1.310	0.08
Kaolinite				3.59	1.00	1.289	0.16
				2.56	0.48	1.240	0.16
Z =				2.50	0.48		
$\text{A}_0 = \text{b}_0 = \text{c}_0 =$				2.34	0.80		
$\text{A} = \text{C} =$				1.99	0.32		
$\text{D} =$				1.90	0.08		
$\text{n} = \text{w} = \text{e} =$				1.85	0.08		

B. A.S.T.M. Index Card for Kaolinite

Remarks: Origin, adsorbed ions and moisture content of A.S.T.M. Kaolinite unknown.

Ring No.	Radius in cm.	Order of Intensity	Interplanar Distance (\AA°)
1	1.225	2	7.18
2	---	--	---
3	2.115	1	4.18
4	2.455	3	3.61
5	3.46	--	2.58
6	3.56	--	2.51
7	3.81	5	2.35
8	---	--	---
9	4.50	--	2.00
10	---	--	---
11	---	--	---
12	6.20	4	1.49

Clay Type: KAOLINITE

Adsorbed Ion: AS-RECEIVED

Remarks: Oven-dry

Ring No.	Radius in cm.	Order of Intensity	Interplanar Distance (A°)
1	1.235	1	7.13
2	2.00	3	4.41
3	2.12	6	4.17
4	2.48	2	3.57
5	3.49	7	2.56
6	3.53	7	2.53
7	3.83	4	2.34
8	3.91	8	2.30
9	4.54	--	1.98
10	----	--	----
11	5.50	--	1.66
12	6.22	5	1.49

Clay Type: KAOLINITE

Adsorbed Ion: AS-RECEIVED

Remarks: Fully hydrated

Ring No.	Radius in cm.	Order of Intensity	Interplanar Distance (\AA°)
1	1.22	2	7.21
2	---	--	---
3	2.115	1	4.18
4	2.465	3	3.59
5	3.46	6	2.58
6	3.56	4	2.51
7	3.85	5	2.33
8	3.87	6	2.32
9	---	--	---
10	---	--	---
11	---	--	---
12	6.18	4	1.49

Clay Type: KAOLINITE

Adsorbed Ion: H

Remarks: Oven-dry

Ring No.	Radius in cm.	Order of Intensity	Interplanar Distance (A°)
1	1.235	1	7.13
2	1.995	3	4.42
3	2.165	6	4.19
4	2.475	2	3.58
5	3.475	7	2.57
6	3.57	7	2.50
7	3.815	4	2.35
8	3.89	8	2.30
9	4.525	9	1.99
10	---	--	---
11	5.475	9	1.67
12	6.185	5	1.49

Clay Type: KAOLINITE

Adsorbed Ion: H

Remarks: Fully hydrated

Ring No.	Radius in cm.	Order of Intensity	Interplanar Distance (\AA°)
1	1.23	1	7.15
2	2.00	3	4.41
3	2.11	6	4.19
4	2.485	2	3.56
5	3.48	7	2.57
6	3.57	7	2.50
7	3.82	4	2.34
8	3.895	8	2.30
9	4.53	9	1.99
10	5.08	9	1.79
11	5.48	--	1.67
12	6.20	5	1.49

Clay Type: KAOLINITE

Adsorbed Ion: CA

Remarks: Fully hydrated

Ring No.	Radius in cm.	Order of Intensity	Interplanar Distance (A°)
1	1.235	1	7.13
2	2.02	3	4.37
3	2.135	6	4.13
4	2.50	2	3.54
5	3.515	5	2.54
6	3.605	5	2.48
7	3.865	4	2.32
8	3.93	--	2.28
9	4.57	--	1.98
10	5.125	8	1.77
11	5.525	9	1.65
12	6.235	7	1.48

Clay Type: KAOLINITE

Adsorbed Ion: NA

Remarks: Oven-dry

Ring No.	Radius in cm.	Order of Intensity	Interplanar Distance (\AA°)
1	1.23	1	7.15
2	2.00	3	4.42
3	---	--	---
4	2.475	6	3.58
5	3.485	2	2.56
6	3.575	7	2.50
7	3.83	7	2.34
8	3.90	4	2.30
9	---	--	---
10	---	--	---
11	---	--	---
12	3.125	5	1.49

Clay Type: KAOLINITE

Adsorbed Ion: NA

Remarks: Fully hydrated

Ring No.	Radius in cm.	Order of Intensity	Interplanar Distance (\AA°)
1	1.23	1	7.15
2	---	--	---
3	2.085	3,2	4.23 4.06
4	2.51	4	3.53
5	---	--	---
6	---	--	---
7	3.85	6	2.33
8	---	--	---
9	---	--	---
10	---	--	---
11	---	--	---
12	6.20	5	1.49

Clay Type: KAOLINITE

Adsorbed Ion: K

Remarks: Oven-dry

Ring No.	Radius in cm.	Order of Intensity	Interplanar Distance (\AA°)
1	1.235	1	7.13
2	2.01	3	4.32
3	2.12	6	4.17
4	2.49	2	3.55
5	3.50	7	2.55
6	3.59	7	2.49
7	3.84	4	2.33
8	3.915	-	2.28
9	4.56	-	1.98
10	----	-	----
11	----	-	----
12	6.23	5	1.48

Clay Type: KAOLINITE

Adsorbed Ion: K

Remarks: Fully hydrated

TYPICAL DIFFRACTION PATTERN OF ILLITE BEARING SHALE

Illinois Illite Bearing Shale: As received
and oven dried at 110°C. for 24 hours

Ring No.	Radius in cm.	Order of Intensity	Interplanar Distance (A°)
1	1.99	2	4.43
2	2.095	3	4.22
3	2.415	9	3.66
4	2.680	1	3.30
5	3.505	4	2.55
6	5.035	5	1.804
7	6.03	6	1.528
8	6.20	8	1.49
9	6.85	7	1.362
10	--	-	--
11	--	-	--
12	--	-	--

No A.S.T.M. Index Card Available



Ring No.	Radius in cm.	Order of Intensity	Interplanar Distance (Å°)
1	1.905	-	5.03
2	2.145	2	4.51
3	2.27	5	4.28
4	2.65	4	3.72
5	2.99	1	3.36
6	----	-	----
7	4.39	-	2.48
8	5.42	-	2.14
9	6.05	-	2.00
10	7.10	6	1.82
11	----	-	----
12	----	-	----

Clay Type: ILLITE

Adsorbed Ion: AS-RECEIVED

Remarks: Fully hydrated

Ring No.	Radius in cm.	Order of Intensity	Interplanar Distance (A°)
1	---	-	---
2	1.995	2	4.42
3	2.05	3	4.31
4	2.36	9	3.75
5	2.625	1	3.38
6	---	-	---
7	---	-	---
8	---	-	---
9	---	-	---
10	5.00	5	1.81
11	5.92	6	1.55
12	6.08	8	1.52
13	6.72	7	1.38

Clay Type: ILLITE

Adsorbed Ion: H

Remarks: Oven-dry

Ring No.	Radius in cm.	Order of Intensity	Interplanar Distance (\AA°)
1	---	-	---
2	1.96	2	4.50
3	2.07	6	4.26
4	---	-	---
5	2.64	1	3.36
6	3.455	3	2.58
7	3.62	-	2.47
8	4.22	-	2.13
9	4.535	-	1.99
10	4.99	4	1.82
11	5.97	7	1.54
12	6.13	5	1.50
13	6.77	8	1.38

Clay Type: ILLITE

Adsorbed Ion: H

Remarks: Fully hydrated



Ring No.	Radius in cm.	Order of Intensity	Interplanar Distance (A°)
1	---	-	----
2	2.15	2	4.50
3	2.26	4	4.29
4	---	-	----
5	2.99	1	3.36
6	4.145	3	2.59
7	4.41	-	2.47
8	5.45	-	2.14
9	5.125	-	1.99
10	7.15	-	1.84
11	---	-	----
12	----	-	----
13	----	-	----

Clay Type: ILLITE

Adsorbed Ion: CA

Remarks: Oven-dry



Ring No.	Radius in cm.	Order of Intensity	Interplanar Distance (A°)
1	1.895	6	5.06
2	2.13	2	4.54
3	2.25	5	4.32
4	2.635	3	3.75
5	2.96	1	3.39
6	4.12	4	2.60
7	4.385	10	2.48
8	5.48	9	2.14
9	6.11	11	1.99
10	7.11	8	1.82
11	----	-	-----
12	----	-	-----
13	----	-	-----

Clay Type: ILLITE

Adsorbed Ion: CA

Remarks: Fully hydrated

Ring No.	Radius in cm.	Order of Intensity	Interplanar Distance (\AA°)
1	---	-	---
2	1.98	2	4.43
3	2.08	3	4.24
4	---	-	---
5	---	-	---
6	3.49	4	2.56
7	---	-	---
8	---	-	---
9	---	-	---
10	5.045	5	1.80
11	5.02	6	1.53
12	6.18	8	1.49
13	6.82	7	1.37

Clay Type: ILLITE
 Adsorbed Ion: NA
 Remarks: Oven-dry



Ring No.	Radius in cm.	Order of Intensity	Interplanar Distance (A°)
1	-----	-	-----
2	2.145	2	4.52
3	2.265	3	4.31
4	-----	-	-----
5	2.995	1	3.36
6	4.155	4	2.59
7	-----	-	-----
8	-----	-	-----
9	-----	-	-----
10	7.13	5	1.33
11	-----	-	-----
12	-----	-	-----

Clay Type: ILLITE

Adsorbed Ion: NA

Remarks: Fully hydrated



Ring No.	Radius in cm.	Order of Intensity	Interplanar Distance (A°)
1	1.90	6	5.03
2	2.125	2	4.55
3	2.235	5	4.34
4	2.63	3	3.75
5	2.965	1	3.35
6	4.105	4	2.60
7	4.39	10	2.48
8	5.44	9	2.14
9	6.115	12	1.99
10	7.115	7	1.82
11	----	-	----
12	----	-	----

Clay Type: ILLITE

Adsorbed Ion: K

Remarks: Oven-dry

Ring No.	Radius in cm.	Order of Intensity	Interplanar Distance (\AA°)
1	---	-	---
2	1.995	2	4.51
3	2.075	3	4.26
4	---	-	---
5	2.645	1	3.28
6	---	-	---
7	3.645	9	2.45
8	4.235	-	2.12
9	4.55	-	1.98
10	4.995	5	1.81
11	5.995	6	1.53
12	6.135	7	1.50
13	6.775	8	1.38

Clay Type: ILLITE

Adsorbed Ion: K

Remarks: Fully hydrated

STRUCTURAL CLASSIFICATION OF THE CLAY MINERALS

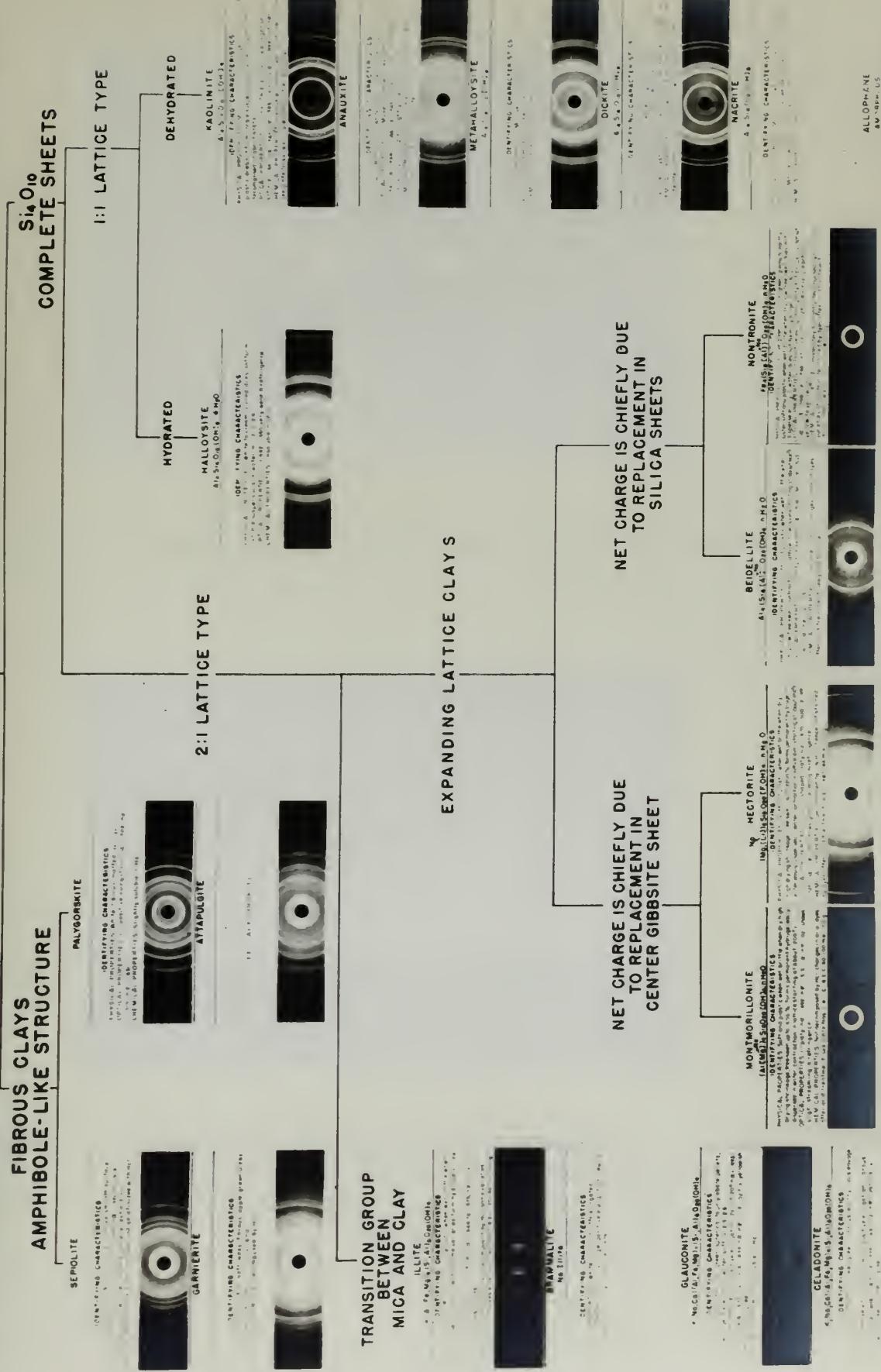


Figure 6.

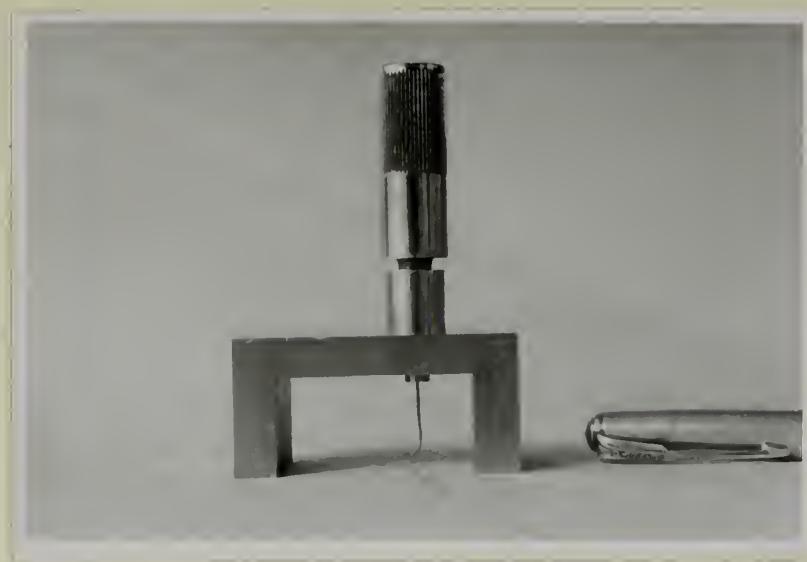


Figure A. Extruding device showing extruded sample



Figure B. Plastic capillary tubing showing:
Tube with forming wire partially withdrawn.
Plastic tubing
Plastic tube, filled and sealed by heat.
Tubes are of 0.5 mm inner diameter.

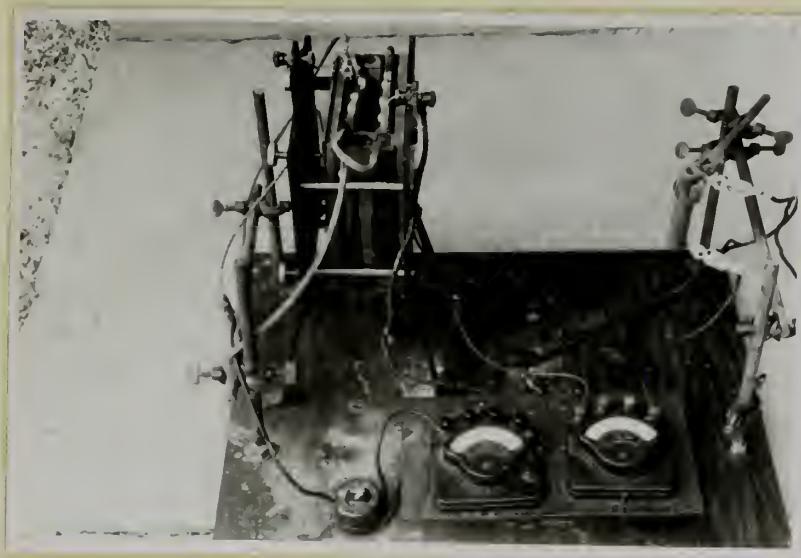


Figure A. Bradfield three cell electrodialyzer

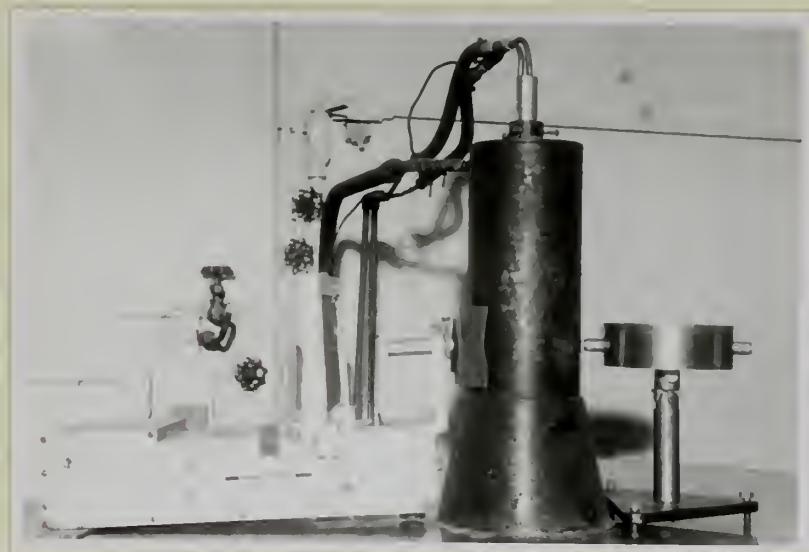
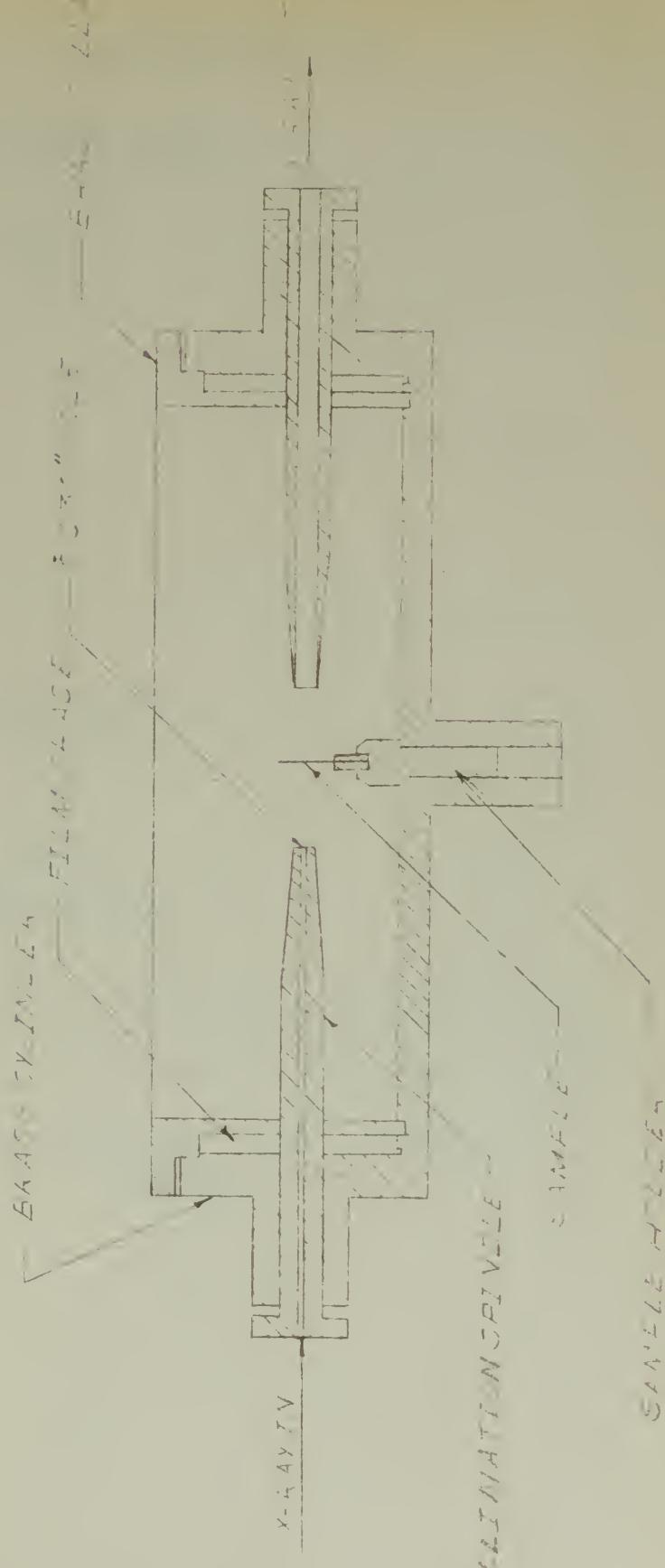


Figure B. X-ray tube and powder cameras
left - Flat cassette and base
right - Debye-Sherrer powder camera



SAMPLE COMPUTATIONS

Debye-Scherrer powder camera:

$$d = \frac{n \lambda}{2 \sin(90^\circ \frac{z}{r})}$$

where n = order = 1

λ = wave length = 1.54 \AA°

z = radius of diffraction ring in question

r = camera radius = 5.7 cm.

d = Interplanar spacing in A° .

for as-received Kaolinite - oven dry $z_{ool} = 1.225 \text{ cm.}$

$$d_{ool} = \frac{1 \times 1.54 \text{ \AA}^\circ}{2 \sin(90^\circ \times 1.225 \text{ cm.})} = 7.18 \text{ \AA}^\circ$$

Flat Cassette Camera:

$$d_{ool} = \frac{n \lambda}{2 \sin(\tan^{-1} \frac{z}{s})}$$

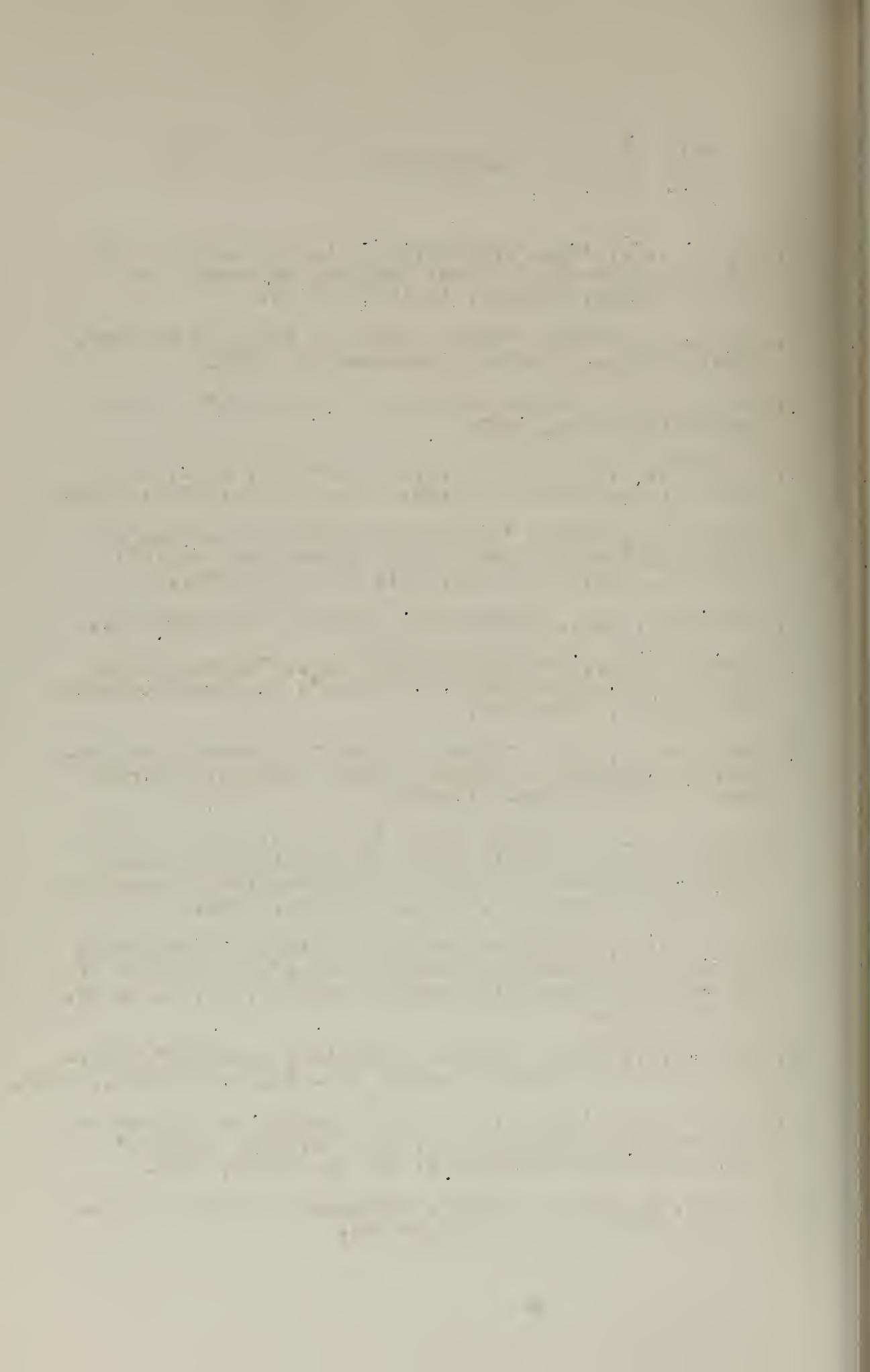
where s = distance from sample to film = 6.0 cm.

For as-received Bentonite-oven dry $z_{ool} = 0.695 \text{ cm.}$

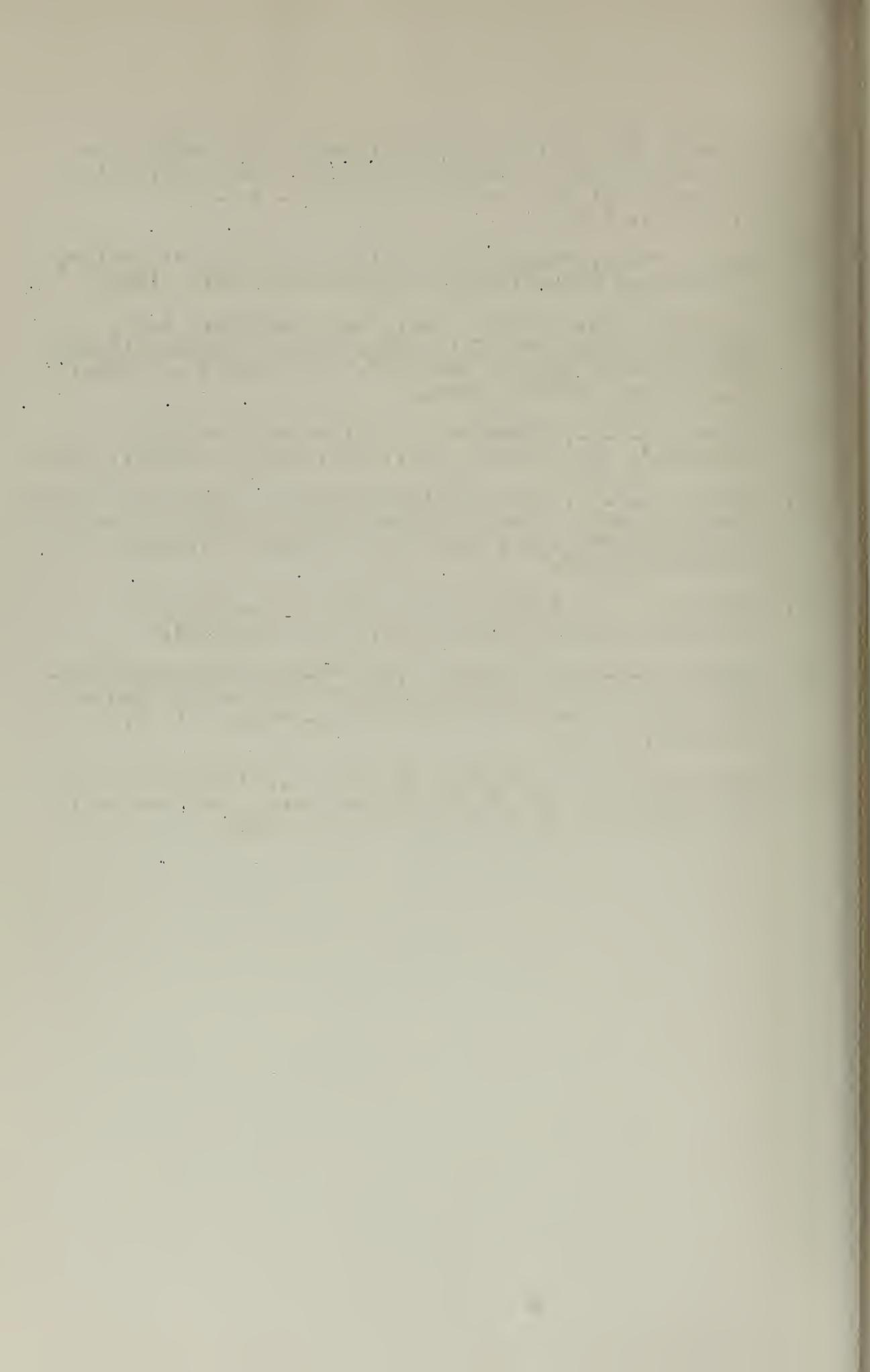
$$d_{ool} = \frac{1 \times 1.54 \text{ cm.}^{-8}}{2 \sin(\tan^{-1} \frac{0.695 \text{ cm.}}{6.0 \text{ cm.}})} = 13.38 \text{ \AA}^\circ$$

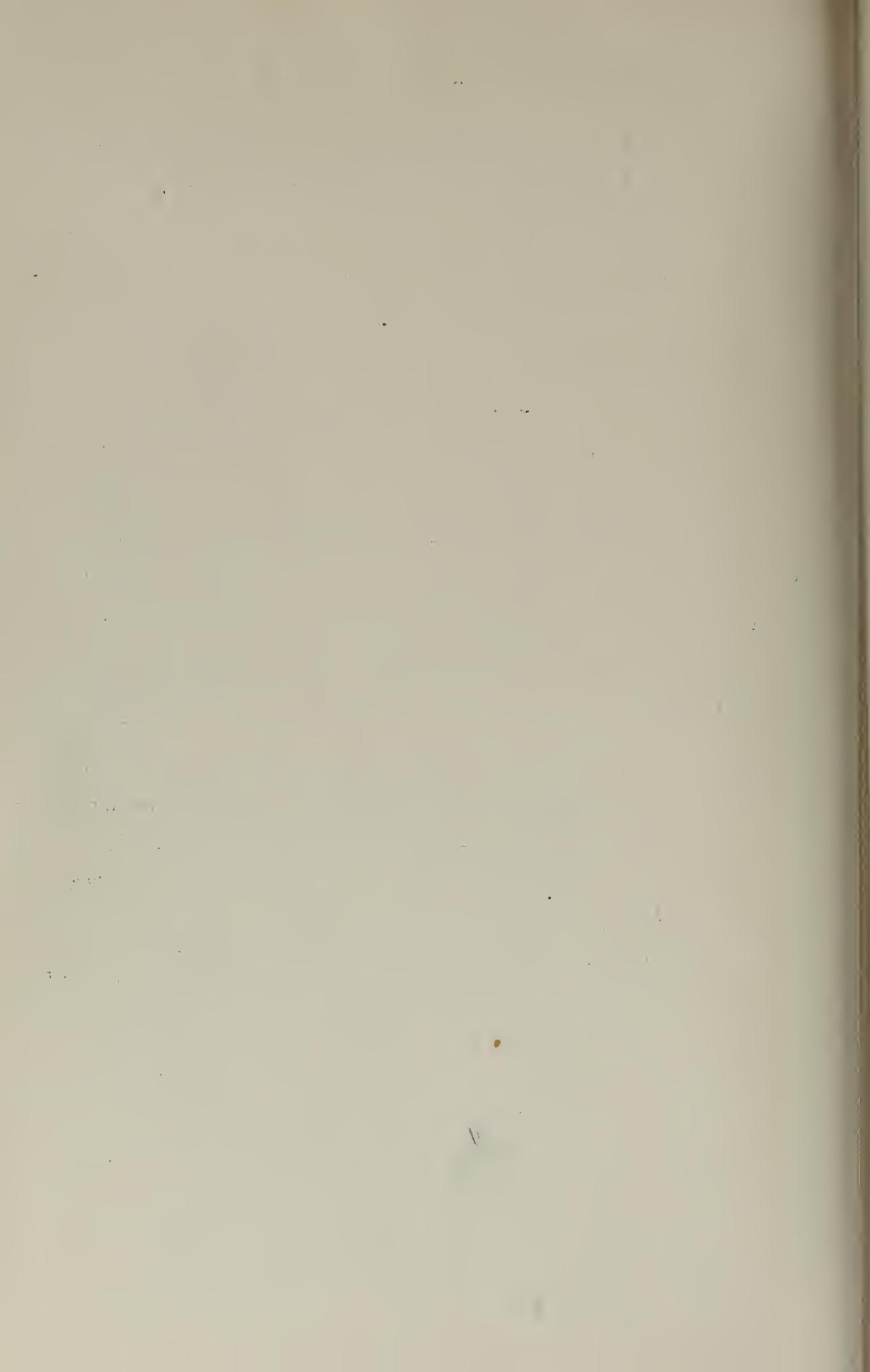
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The identification and in-
vestigation of the expansion
characteristics of clays by x-ray
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